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US 4233361 A
WPI Abstract Accession No. 1989-071717 &
JP01-022938A (NAGOYA) 25.01.1989 (see abstract)

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(54) Abstract Title
Fire stable expanded polystyrene foam materials

(57) Low flammability fire stable expanded foam blocks, panels or mouldings are produced by coating expanded polystyrene spheres in a mixture of liquid resol phenolic resin, low viscosity phosphorus and / or chlorinated flame retardants and acid partial phosphate ester of carbonific polyols and cured by the introduction of steam into the mixture contained in rigid moulds. The mixture should produce a phosphorus content in the cured mass of above 3% and contain phenolic resins at greater than 25% of the total weight of components of the mixture. The flame retardant system is caused to both penetrate and surround the polystyrene spheres.

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FIRE STABLE EXPANDED POLYSTYRENE FOAM MATERIALS

The present invention concerns the manufacture of polystyrene composite materials which retain a degree of integrity when exposed to fire regimes, and have significantly reduced flammability. These foams are intended to be used in structures in which fire barriers are required that are thermal insulants but resistant to fire.

Conventionally, expanded polystyrene foam in slab form is generally used as an insulant in building construction and particularly as the core of insulating sandwich panels and walls, typically in refrigeration applications. The skins of such walls or panels are generally thin precoated steel. The structures may be assembled by the use of adhesives or mechanical fastenings or a combination of both. The foam block may also be used as thermal insulation in building construction.

The conventional process for the production of polystyrene foam slab or forms is as follows :-

- (a) Unexpanded polystyrene is supplied from the manufacturer in granular form graded for particle size. This granular polystyrene has a proportion of pentane dissolved in it.
- (b) The grains are exposed to heat, usually by steam in a tall fluidised bed. As the grains pass from the bottom of the fluidised bed to the top, they soften and as the pentane is lost from solid solution, the released gas causes the softened polystyrene granules to expand up to fifty times the original volume. The grains become approximately spherical beads with a very low density. The expanded polystyrene bead is collected at the top of the bed. The beads still contain a small amount of pentane after this primary expansion process.
- (c) The dry beads are introduced into moulds with walls penetrated by many small apertures leading to plenum chambers behind each wall. The charge may be compressed. Steam at pressures not exceeding 1.5 bar is introduced into the vessel containing the polystyrene bead. The polystyrene granules soften and the residual pentane is released. In this second stage the volume expansion of the charge is contained by the mould walls forcing the beads together and fusing them to form a single light weight mass of expanded polystyrene foam.
- (d) If the mould was in the form of a block, the blocks of expanded polystyrene are subsequently sliced into slabs. These slices are used as the cores of the insulating walls or panels mentioned in above.

In this current invention the process described above is modified by coating the expanded beads derived from the primary expansion as in (b), with mixtures of phenolic resin containing dissolved flame retardants and acidic partial phosphate esters of carbonific polyols. The expanded polystyrene beads, coated with the resin mixture are introduced into the moulds and exposed to the same steam heating cycle as is described in (c) above. As the polystyrene beads expand through the phenolic resin mixture, some of the phenolic resin and the dissolved flame retardants (which include the acid phosphate curing system) become dissolved in the polystyrene, forming a polymer alloy. The remainder of the cured phenolic system forms a matrix at the boundary of expansion of each bead. Thus the steam not only causes the polystyrene to expand as is conventional but also causes the phenolic resin system to cure to a solid and acts to cause some of the flame retardants to permeate into the polystyrene.

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When the polystyrene phenolic produced as above is exposed to heat and fire regimes an entirely different behaviour is observed as compared with unmodified expanded polystyrene. A proportion of the polystyrene may pyrolise to volatile flammable fractions which will combust in the fire regime, but this effect is reduced by a proportion of the flame retardants producing non flammable volatile gases. However, the main effect of the invention is that the high phosphorus level achieved by the process together with the presence of the phenolic resins causes a flame resistant insulating char, consisting of a hollow residual matrix, to be produced at the fire exposed surface. This insulating char significantly reduces the combustion of the underlying layers. Further, it prevents the underlying layers of the solid material from melting and subsequently dripping into the fire regime, as is commonly observed during the combustion of conventional expanded polystyrene foam.

With respect to the prior art, expanded polystyrene bead and phenolic resin have been previously combined to produce fire retardant panels and structures by a variety of methods, all requiring the preparation of the structures by attempting to fill the voids between the spherical beads with foamed or cold cured phenolic resin.

US patent 4,233,361 (ARCO 11/1980) reveals insulating polystyrene/phenolic panels whereby a foaming resol phenolic resin is foamed round the expanded polystyrene bead and the foaming action is promoted by the use of strong acids. EP 0832919A1 reveals a similar material in which pre expanded polystyrene spheres are coated with phenolic resins and cured with microwaves. SA 876051 reveals a similar system whereby the pre expanded polystyrene spheres are coated with a foamed phenolic resin and cured.

All of these preceding production systems present practical difficulties in production terms given the scale and quantity of polystyrene block that is require. Further, all these previous embodiments require a step or process beyond that which is conventional. The utility of this current invention is that the flame resistant polystyrene block is produced from the same equipment, and within the same process times as is used in conventional production.

The novelty of the current invention lies in the combination of the process with the formulation designed to act in concert with this conventional steam curing. Neither the penetration of the flame retardants into the expanded polystyrene nor the promotion of the rigid char forming layers can be achieved by the low temperature curing systems revealed in the prior art.

With respect to the prior art, application EP 92309426.2 (BPC) reveals a method of cold curing phenolic resins with partial phosphate esters of carbonific polyols derived from a method revealed in AT A 1790-91 (CFB), the work of the current author. In this current invention the same or similar phosphate esters are used to promote the cure of the phenolic resins but at far higher levels than envisaged in EP 92309426.2 as the curing agent is used to raise the level of phosphorus in order to impart flame retardancy.

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In this current invention the phenolic resin may be any liquid resol phenolic resin, but is preferably a non aqueous resol phenolic resin as described in GB 2291881 (current author). These materials are typified by the absence of water but the presence of di ethyl ethyl phosphonate as a non reactive diluent. As a proportion of water remains in the expanded polystyrene block after final expansion, and water is produced from the condensation polymerisation of the phenolic resin, aqueous resol phenolic resins used in the specified procedure will leave yet more water in the cured block. In practice wet block is allowed to age before sectioning and machining. The use of aqueous phenolic resins will greatly extend this maturing period.

In this current invention additional low viscosity phosphate or phosphonate ester flame retardants are added to the phenolic resin. These may be diethyl ethyl phosphonate, di-methyl methyl phosphonate, tri-chloro ethyl phosphate, tri ethyl phosphate, tri chloromethyl phosphate or any other aliphatic low viscosity liquid phosphate or phosphonate ester providing the ester has no more than two carbon atoms. This low viscosity phosphate ester may be used to dissolve and disperse chlorinated paraffin flame retardants, that are not compatible with phenolic resin.

The acid partial phosphate ester curing agent is added to this mixture. The curing system is a liquid partial phosphate ester of carbonific polyols. A suitable product is the commercial product Budit 380 (Chemische Fabrik Budenheim). This or any other partial phosphate ester produced by the methods given in AT A 1790-91 is suitable for use in the system. Other acidic phosphate esters of carbonific polyols will function adequately within this system providing the acid value is greater than 300 mgs KOH/gm and the phosphorus content exceeds 17%.

The invention may be best illustrated and specified with reference to the following examples. Using any of the formulations as shown in table 1 the chlorinated paraffin, where used, is dissolved by stirring into the liquid phosphate plasticiser. This mixture is added to the phenolic

Table 1							
Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
9 mm expanded polystyrene spheres	24.5	24.5	24.5	24.5	24.26	24.5	24.5
3 mm expanded polystyrene spheres					0.24		
Non aqueous phenolic resin ⁽¹⁾	15.1	12.5	13.7	13	15.1		15.1
Aqueous phenolic resin ⁽²⁾						15.1	
Di ethyl ethyl phosphonate	1.52	4.56	2		1.52	3.48	
Tri chloro ethyl phosphate				6.5			3.02
70% Chlorinated paraffin		1.4	2.27				0.82
Partial phosphate ester ⁽³⁾	7.56	5.96	6	4.9	7.56	7.56	6
Specific gravity (kgms/M ³)	34	41	41	41	43	40	42
thermal conductivity K value	15	17.5	17.5	22	18	18	19
compressive strength MPA	0.83	0.66	0.67	0.86	0.84	0.69	0.58
Brandshaft rating (DIN 4102)	B2	B1/2	B1	B1!	B2	B2	B1/2

(1) Represented by HMC IR5393 (2) Represented by Borden Cellobond 2027L

(3) Represented by Chemische Fabrik Budenheim Budit 380

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resin and stirred. The partial phosphate ester is then added to the phenolic resin. If the mixed components are maintained at ambient temperature the mixture has a pot life of up to four hours except where aqueous borne phenolic resins are used, as in example 6, where the pot life may be no more than 30 minutes.

The polystyrene bead is selected fresh from the primary expander, typically containing 2 to 5 % residual pentane. The weights given in table 1 are sufficient for one cubic metre of flame retarded foam. The phenolic flame retardant mixture is stirred into the expanded polystyrene spheres using a planetary paste mixer (dough mixer), a ribbon blender, or any other such low speed mixer capable of giving a tumbling action. The mixing is continued until the polystyrene spheres are evenly coated with the phenolic flame retardant mixture when the mass is then introduced into the mould. Some compression may be applied to compact the mould charge if required.

Steam is introduced into the mould, in the same manner and time cycle as is conventional when using that mould for non flame retarded product. The block or form is removed from the mould and allowed to mature in the normal manner, whereby the residual water is gradually lost from the product. If the product is a block mould product which is conventionally reduced to panels, it may not be cut with hot wires but must be cut with abrasive wire or band saws.

Scrap crumb or aged expanded polystyrene bead may be used but a significant degree of charge compression will be needed to ensure adequate coherence of the moulding.

The example formulations 1 to 7 table 1 above show that in all cases the polystyrene foam has a significant increase in physical strength of between 2 and 3 times that of unmodified expanded polystyrene foam with only minor increase in thermal conductivity. In all cases conventional expanded polystyrene foam is considered flammable when exposed to testing under the DIN 4102 Brandshaft conditions. Similar results are obtained using the BS 476 part 7 measure. The unmodified expanded polystyrene foam is unclassifiable.

In contrast the modified foam gives flame spread ratings between classes 1 and 3. Similar enhanced fire performance results are obtained providing that at all times the weight of the modifying phenolic resin mixture, including neutral and partial phosphate esters, is above 40% of the weight of expanded polystyrene spheres, and the resin mixture contains components to give a phosphorus content of above 6%, thus providing a minimum phosphorus content of 3% to the whole mixture. Likewise, the phenolic resin content should generally be above 25% of the entire mixture. Below this level insufficient char stability will be observed.

Under conventional fire test measures a degree of combustion (flame spread) is observed, but less so in the presence of chlorine containing flame retardants such as in examples 4 and 7 in table 1 . The residual char forms an open cell structure capable of preventing further penetration of the combustion and of supporting itself without melting or dripping molten polystyrene.

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Likewise when the modified polystyrene foam is used as an insulating core between non flammable skins and exposed to a cellulosic fire test as a barrier panel, the polystyrene may produce some smoke from anaerobic pyrolysis but the char will remain in place to support the skins and retain the integrity of the fire barrier.

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CLAIMS.

- 1) A process for the production of low flammability fire stable expanded polystyrene foam blocks, panels or mouldings whereby the expanded polystyrene spheres are coated in a mixture of liquid resol phenolic resin, low viscosity phosphorus and/or chlorinated flame retardants and acid partial phosphate ester of carbonific polyols and cured by the introduction of steam into the mixture contained in rigid moulds. The mixture must produce a phosphorus content of the cured mass of above 3% and contain phenolic resins at greater than 25% of the total weight of components of the mixture.
- 2) A process as in claim 1) where the phenolic resin is a non aqueous phenolic resin in which the non reactive diluent is di ethyl ethyl phosphonate.
- 3) A process as in claims 1) and 2) where the liquid flame retardant is di ethyl ethyl phosphonate.
- 4) A process as in claims 1) and 2) where the liquid flame retardant is tri chloro ethyl phosphate.
- 5) A process as in claims 1) and 2) where chlorinated paraffin is dissolved in the liquid flame retardant.
- 6) Composite structures where the low flammability, fire stable expanded foam as in claim 1) to 5) inclusive, is used as the core of sandwich panels with non flammable skins.



INVESTOR IN PEOPLE

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Claims searched: 1 to 6

Examiner: R.J.MIRAMS
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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.R): B2E (EFA, EFBB, EFE, EFJ, ER).
Int Cl (Ed.7): B29C, C08J 9/22, 9/224, 9/228, 9/232, 9/236.
Other: ONLINE: WPI, EPODOC, JAPIO.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB1601013A (SICCA)	
A	EP0832919A1 (KNAUF)	
A	EP0539098A1 (BP INTERNATIONAL)	
A	US4714715A (MOSIER)	
A	US4623584A (MASUI)	
A	US4233361A (FULTZ)	
A	FR2354186A (SAUNIER)	
A	WPI Abstract Accession No.1989-071717 & JP01-022938A (NAGOYA) 25.01.1989 (see abstract)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.